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FLAME RETARDANT LOW SPECIFIC GRAVITY UNSATURATED POLYESTER RESIN COMPOSITION
[NANNENSEI TEIHIJUU FUHOUWA PORIESUTERU SHIBOU SOSEIBUTSU]

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[Scope of Claim(s)]

[Claim 1] A flame retardant low specific gravity unsaturated polyester resin composition that is characterized in that it contains 300 parts by weight of an aluminum hydroxide and 30 to 70 parts by weight of a hollow filler as an inorganic filler based on 100 parts by weight of an unsaturated polyester resin and a cross-linking agent.

[Claim 2] The flame retardant low specific gravity unsaturated polyester resin composition recited in Claim 1 wherein said hollow filler has a pressure resistance of 2100×10^4 N/m^2 or greater and a true specific gravity in the range 0.3 to 0.6.

[0001]

[Technical Field of the Invention] The present invention relates to a flame retardant, low specific gravity unsaturated polyester resin composition. More particularly, the present invention relates to a flame retardant, low specific gravity unsaturated polyester resin composition that has flame retardancy while having a molded article specific gravity of 1.6 or less and that has excellent dimensional accuracy, heat resistance, mechanical strength, and moldability.

[0002]

[Prior Art] Conventionally, unsaturated polyester resin compositions (bulk molding compounds) have excellent dimensional accuracy, heat resistance, mechanical strength, and moldability, so that they are widely used in fields in which dimensional accuracy is strict and flame retardancy is required, such as OA equipment, chassis for office equipment, etc.

[0003] However, while molded articles having excellent dimensional accuracy, flame retardancy, mechanical strength, and heat resistance can be obtained with conventional unsaturated polyester resin compositions using cured molding on the one hand, problems of increased specific gravity of the molded article due to the amount of inorganic filler and fiber reinforcement contained in order to retain these excellent properties have appeared. Also, as the specific gravity of molded articles become higher even compared to thermoplastic resins, the area of use thereof has been restricted so far. In a general HB grade BMC, a low specific gravity can be obtained easily because hollow fillers can be added freely, but in a flame retardant BMC, a low specific gravity is difficult because a certain amount of aluminum hydroxide must be added.

[0004] An object of the present invention is to provide a flame retardant low specific gravity unsaturated polyester resin composition that attains a low specific gravity while maintaining the excellent flame retardancy, dimensional accuracy, heat resistance, mechanical strength, and moldability characteristics possessed by conventional flame retardant low specific gravity unsaturated polyester resin compositions.

[0005]

[Means for Solving the Problem(s)] As a result of earnest investigation to achieve the aforementioned object, the inventors of the present invention have found that a flame retardant low specific gravity unsaturated polyester resin composition that has a low specific gravity and excellent flame retardancy, dimensional accuracy, heat resistance, mechanical strength, and moldability can be obtained by adding aluminum hydroxide and hollow fillers that are mixed ate certain ratios to a low specific gravity unsaturated polyester resin composition and have completed the present invention.

[0006] That is, the present invention provides a flame retardant, low specific gravity unsaturated polyester resin composition that is characterized in that it contains 300 parts by weight of an aluminum hydroxide and 30 to 70 parts

by weight of a hollow filler as an inorganic filler based on 100 parts by weight of an unsaturated polyester resin and a cross-linking agent. Further, the present invention provides a flame retardant low specific gravity unsaturated polyester resin composition wherein the aforementioned hollow filler has a pressure resistance of 2100 x 10^4 N/m^2 or greater and a true specific gravity in the range 0.3 to 0.6.

[0007] The kind of unsaturated polyester resin used in the present invention is not especially limited. For the unsaturated polyester resin used in the present invention, appropriate resins which polycondense a polyalcohol with an unsaturated polybasic acid and a saturated polybasic acid and that are usually used as a molded material can be used. Also, a vinyl ester resin and a diallyl phthalate resin may be blended as a part of the unsaturated polyester resin.

[0008] Examples of polyalcohols which can form the unsaturated polyester resin include ethylene glycol, propylene glycol, butane diol, diethylene glycol, dipropylene glycol, triethylene glycol, pentanediol, hexanediol, neopentanediol, hydrogenated bisphenol A, bisphenol A, glycerin, etc.

[0009] Examples of the unsaturated polybasic acid include maleic anhydride, fumaric acid, citraconic acid, itaconic

acid, etc. Also, examples of the saturated polybasic acid include phthalic anhydride, isophthalic acid, terephtalic acid, chlorendic acid, succinic acid, adipic acid, sebacic acid, tetrachloro phthalic anhydride, tetrabromo phthalic anhydride, endmethylenetetrahydro phthalic anhydride, etc.

[0010] As the crosslinking agent, appropriate agents having a polymeric double bond which can polymerize with the aforementioned unsaturated polyester can be used. Examples of the crosslinking agent include styrene monomer, diallyl phthalate monomer, diallyl phthalate prepolymer, methyl methacrylate, triallyl isocyanurate, etc. The amount of the crosslinking agent is 25 to 70 parts by weight, preferably 35 to 65 parts by weight, based on 100 parts by weight of the unsaturated polyester resin and the crosslinking agent.

[0011] The inorganic filler used in the present invention is aluminum hydroxide and its form, etc., is not especially limited, but preferably, it has an average particle size of 1.8 μm to 50 μm. If the average particle size of the inorganic filler is less than 1.8 μm, the viscosity becomes high and it cannot be manufactured. If the average particle size of the inorganic filler is more than 50 μm, the fluidity of the material decreases and the moldability decreases. Preferably, the particle size distribution has a broad peak as a filler.

[0012] The amount of the inorganic filler is 300 parts by weight or more based on 100 parts by weight of the unsaturated polyester and the crosslinking agent. If the amount of the inorganic filler is less than 300 parts by weight, flame retardancy is not conferred. Preferably, the amount of the

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inorganic filler is 350 to 400 parts by weight based on 100 parts by weight of the unsaturated polyester and the crosslinking agent.

[0013] As another inorganic filler powder, material such as calcium carbonate, wallastonite, clay, talc, mica, silicic acid anhydride, etc. can be used according to need, but an amount that is less than 10 percent by weight based on the total amount of inorganic filler is preferred.

[0014] The hollow filler used in the present invention is not especially limited and examples include glass balloon, silica balloon, alumina balloon, etc. As attributes of the hollow filler, a pressure resistance of 2100 x 10^4 N/m^2 and a true specific gravity of the range 0.3 to 0.6 are preferred. More preferably, the pressure resistance is in the range 2100 x 10^4 N/m^2 to 3500 x 10^4 N/m^2 and the true specific gravity is in the range 0.35 to 0.55. If the pressure resistance is less than 2100 x 10^4 N/m^2, the hollow

filler is destroyed in production steps and molding steps and the specific gravity of the molded article cannot become low. If the true specific gravity is less than 0.3, the viscosity increases, so that the addition amount of the aluminum hydroxide should be decreased, and flame retardancy is not conferred and the moldability decreases. Reversely, if the true specific gravity is more than 0.6, the specific gravity of the molded article does not become low.

[0015] The amount of the hollow filler is 30 to 70 parts by weight based on 100 parts by weight of the unsaturated polyester resin and the crosslinking agent. If the amount of the hollow filler is more than 70 parts by weight, the viscosity increases, the viscosity increases, so that the addition amount of the aluminum hydroxide should be decreased, flame retardancy is not conferred, and problems with the moldability arise. Reversely, if the amount of the hollow filler is less than 30 parts by weight, the specific gravity of the molded article becomes high. The preferred amount is 40 to 60 parts by weight.

[0016] In the unsaturated polyester resin composition according to the present invention, if necessary, low constrictive agents, curing agents, mold lubricants, thickeners, fiber reinforcements, pigments, viscosity

decreasing agents, etc. may be used together with the above ingredients. Further, if the amount of aluminum hydroxide added is greater than 300 parts by weight and it is difficult to add a hollow filler, thinners may be used as necessary.

[0017] As the low constrictive agent, one or more thermoplastic polymers which are generally used as low constrictive agents such as polystyrene, polymethyl methacrylate, polyvinyl acetate, saturated polyester, styrene-butadiene type rubber, etc. can be used.

[0018] Examples of the curing agent include t-butyl peroxyoctoate, benzoyl peroxide, 1,1-di-t-butylperoxy-3,3,5-trimethyl cyclohexane, t-butylperoxyisopropylcarbonate, t-butylperoxybenzoate, dicumylperoxide, di-t-butylperoxide, etc.

[0019] As the mold lubricant, for example, stearic acid, zinc stearate, calcium stearate, aluminum stearate, magnesium stearate, carnauba wax, etc. can be used in appropriate amounts.

[0020] Examples of the thickener include metal oxides such as magnesium oxide, magnesium hydroxide, calcium hydroxide and calcium oxide, etc., and isocyanate compounds. The thickener need not always be used.

[0021] As the fiber reinforcement, chopped strand glass cut to about 1.5 to 25 mm fiber length can be used. Also, organic and inorganic fibers such as pulp fiber, Tetoron (registered trademark) fiber, vinylon fiber, carbon fiber, aramid fiber, wallastonite, etc., can be used.

[0022] The method of manufacturing the flame retardant low specific gravity unsaturated polyester resin composition according to the present invention constituted by the aforementioned ingredients is not especially limited, but for example, compression molding, transfer molding, injection molding, etc., can be adopted to obtain the desired molded articles. Molded articles that demonstrate excellent flame retardancy at a low specific gravity of 1.6 and have excellent dimensional accuracy, heat resistance, mechanical strength, etc., can be obtained.

[0023]

[Examples] The present invention will now be explained with reference to Examples and Comparative Examples. Also, the present invention is not limited by the following Examples.

[0024] (Examples 1 - 10) The addition ingredients and those amounts shown in Table 1 were mixed by using a double-cup type kneader at to obtain unsaturated polyester resin compositions. Here, the used unsaturated polyester resin comprises fumalic acid/propylene glycol/hydrogenated

bisphenol A at the ratio of 100 mol/80 mol/20 mol with 45% by weight of a styrene monomer as a crosslinking agent.

[0025] These compositions were evaluated for molding shrinkage ratio, specific gravity, flame retardancy, moldability, surface smoothness and production availability. The method of testing and evaluation was as follows.

[0026] (1) Molding Shrinkage Ratio

Shrinkage disks defined in JIS K6911 were obtained by compression molding at a molding temperature of 150° C. under a molding pressure of 10 MPa for a molding time of 3 minutes. Then, the molding shrinkage ratio was calculated based on JIS K6911.

[0027] (2) Specific Gravity

(2)-1 Specific gravity of the compression molded articles

The shrinkage disks defined in JIS K6911 were obtained by molding at a molding temperature of 150° C. under a molding pressure of 10 MPa for a molding time of 3 minutes. After a test piece was obtained by cutting the shrinkage disk, the specific gravity was measured based on JIS K6911.

(2)-2 Specific Gravity of the Injection Molded Articles

The injection molding was carried out by using an injection molding machine (Niigata Tekkousho Co., Ltd.; NNT250PSCH 7000) in the Test box (360 x 120 x 25 mm, wall thickness: 4 mm in a long edge side, 5 mm in a short edge side, 3 mm in

a bottom) at a molding temperature of 160° C. under an injection pressure of 30 MPa for a molding time of 2 minutes. After test pieces were obtained by cutting the molded article, the specific gravity was measured based on JIS K6911.

[0028] (3) Flame retardancy

Test pieces defined in UL94 (20 mm vertical flammability test V-0) were obtained by molding at a molding temperature of 150° C. under a molding pressure of 10 MPa for a molding time of 3 minutes. The flammability was measured based on UL94 (20 mm vertical flammability test V-0). The evaluations are indicated by the symbols O: V-0 at a molded article thickness of 1.2 mm or less; O: V-0 at a molded article thickness of 3 mm or less; and x: V-0 at a molded article thickness of 3 mm or greater or did not attain V-0 in the table.

[0029] (4) Moldability

The injection molding was carried out by using an injection molding machine (Niigata Tekkousho Co., Ltd.; NNT250PSCH 7000) in the Test box explained in (2)-2 Specific Gravity of the Injection Molded Articles above at a molding temperature of 160° C. under an injection pressure of 30 MPa for a molding time of 2 minutes. Leveling, glossiness, and filling were visually evaluated. The evaluations are

indicated by the symbols ⊙: very good; ○: good; Δ: inferior; and x: defect in the table.

[0030] The results of these evaluations are shown in Table 1. As shown in Table 1, destruction of the hollow filler in production steps and molding steps was extremely low and stable, and molded articles that a molded article specific gravity of 1.8 or less and that had excellent flame retardancy, moldability, and dimensional accuracy were obtained.

[0031]

[Table 1]

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Unsaturated polyester resin	55	55	55	55	55	55	55
Polystyrene 40 wt % solution [1)]	75	75	75	75	75	75	75
t-butylperoxybenzoate	3	3	3	3	3	3	3
Aluminum hydroxide (average particle size: 8 μm)	350	350	350	300	400	350	350
Glass balloon (pressure resistance: 2200 x 10^4 N/m^2, true specific gravity: 0.45)	30	50	70	50	50	-	-
Glass balloon (pressure resistance: 2200 x 10^4 N/m^2, true specific gravity: 0.30)	-	-	-	-	-	50	-
Glass balloon (pressure resistance: 2200 x 10^4 N/m^2, true specific gravity: 0.60)	-	-	-	-	-	-	50
Zinc stearate	8	8	8	8	8	8	8
Chopped glass (6.0 mm)	70	70	70	70	70	70	70
Carbon black	2	2	2	2	2	2	2
Molding shrinkage ratio (%)	0.02	0.00	-0.03	0.01	-0.02	0.00	0.00
Specific gravity of compression molded article	1.55	1.48	1.43	1.45	1.48	1.45	1.53
Specific gravity of injection molded article	1.58	1.51	1.47	1.49	1.51	1.48	1.56

Flame retardancy [2]	O	O	O	O	O	O	O
Moldability [3]							
Leveling	O	O	O	O	O	O	O
Glossiness	O	O	O	O	O	O	O
Filling	O	O	O	O	O	O	O
Production availability	Available	Available	Available	Available	Available	Available	Available

[0032]

[Table 2] /3

Table 1 (continued)

	Ex. 8	Ex. 9	Ex. 10
Unsaturated polyester resin	55	55	55
Polystyrene 40 wt % solution [1]	75	75	75
t-butylperoxybenzoate	3	3	3
Aluminum hydroxide (average particle size: 8 μm)	350	300	350
Glass balloon (pressure resistance: 2200 x 10^4 N/m^2, true specific gravity: 0.25)	50	30	–
Glass balloon (pressure resistance: 2200 x 10^4 N/m^2, true specific gravity: 0.73)	–	–	50
Zinc stearate	8	8	8
Chopped glass (6.0 mm)	50	50	50
Carbon black	2	2	2
Molding shrinkage ratio (%)	0.00	0.03	0.01
Specific gravity of compression molded article	1.43	1.50	1.57

Specific gravity of injection molded article	1.47	1.56	1.60
Flame retardancy [2]	O	O	O
Moldability [3]			
Leveling	O	O	O
Glossiness	O	O	O
Filling	O	O	O
Production availability	Available	Available	Available

[1] Styrene content: 60 wt %

[2] The meaning of the symbols are as follows:

O: V-0 at a molded article thickness of 1.2 mm or less;

O: V-0 at a molded article thickness of 3 mm or less;

x: V-0 at a molded article thickness of 3 mm or greater or did not attain V-0

[3] The meaning of the symbols are as follows: O: very good; O: good; Δ: inferior; and x: defect

[0033] (Comparative Examples 1 - 8) In Comparative Examples 1 - 8, the addition ingredients and those amounts shown in Table 2 were used as in Examples 1 - 10. The ingredients were mixed by using a double-cup type kneader to obtain unsaturated polyester resin compositions.
Further, the molding shrinkage ratio, specific gravity, flame retardancy, moldability, and production availability were evaluated.

[0034] These results of this measurement evaluation are shown in Table 2. As shown in Table 2, in unsaturated polyester resin compositions in which the amount of the hollow filler was outside the range specified above, moldability and flame retardancy were remarkably worse, and reversely, when insufficient, molded articles that satisfied the molded article specific gravity could not be obtained. In unsaturated polyester resin compositions in which the pressure resistance of the hollow filler was less than the aforementioned specified values, the hollow filler was destroyed in production steps and molding steps and the molded article specific gravity became high, and in unsaturated polyester resin compositions in which the amount was increased, molded articles that had satisfactory flame retardancy could not be obtained.

[0035] In unsaturated polyester resin compositions in which the amount of the aluminum hydroxide did not satisfy the ratio specified above, flame retardancy was remarkably worse.

[0036]

[Table 3]

Table 2

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Unsaturated polyester resin	55	55	55	55	55	55	55	55
Polystyrene 40 wt % solution [1]	75	75	75	75	75	75	75	75
t-butylperoxybenzoate	3	3	3	3	3	3	3	3
Aluminum hydroxide (average particle size: 8 μm)	350	350	300	270	350	350	350	250
Glass balloon (pressure resistance: 2200 x 10^4 N/m^2, true specific gravity: 0.45)	20	80	80	80	-	-	-	-
Glass balloon (pressure resistance: 1600 x 10^4 N/m^2, true specific gravity: 0.45)	-	-	-	-	50	70	100	100
Zinc stearate	8	8	8	8	8	8	8	8
Chopped glass (6.0 mm)	70	70	70	70	70	70	70	70
Carbon black	2	2	2	2	2	2	2	2
Molding shrinkage ratio (%)	0.03	-	- 0.02	0.00	0.02	0.01	-	0.00
Specific gravity of compression molded article	1.62	-	1.45	1.42	1.67	1.63	-	1.58
Specific gravity of injection molded article	1.66	-	1.48	1.45	1.70	1.66	-	1.55
Flame retardancy [2]	O	-	O	X	O	O	-	X
Moldability [3]								
Leveling	O	-		O	O	O	-	X
Glossiness	O	-	O	O	O	O	-	X

	Filling	O	-	X	X	O	O	-	X
Production availability		Available	Not Available	Available	Available	Available	Available	Not Available	Available

[0037]

[Effect of the Invention] The present invention provides a flame retardant low specific gravity unsaturated polyester resin composition that attains a low specific gravity while maintaining the excellent flame retardancy, dimensional accuracy, heat resistance, mechanical strength, and moldability characteristics possessed by conventional flame retardant low specific gravity unsaturated polyester resin compositions, and the aforementioned composition, and as a result its low specific gravity and excellent flame retardancy that cannot be obtained with the prior art, it is extremely practical in fields in which dimensional

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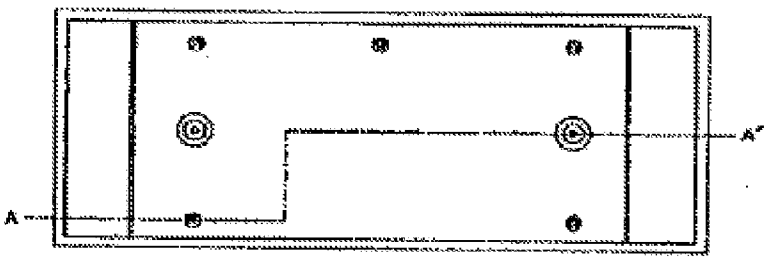
accuracy is strict and flame retardancy and light weight are required, such as OA equipment, chassis for office equipment, etc.

[Brief Description of the Drawings]

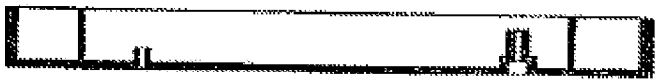
[Figure 1] This is a plane section of a the Test box used in the Examples.

[Figure 2] This is a cross-section A - A' of Figure 1.

[Fig. 1]



[Fig. 2]



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